PERFORMANCE OF INTEGRATED TREATMENT SYSTEM OF PHOTO-FENTON AND MEMBRANE BIOREACTOR FOR SYNTHETIC SPENT CAUSTIC WASTEWATER

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ABSTRACT

The potential of a combined integrated treatment system using photo-Fenton process and membrane bioreactor (MBR) was studied in the treatment of spent caustic wastewater with initial COD and sulfide of 1990-2740 mg/L and 82-165 mg/L, respectively and at biodegradability level (BOD_5/COD) of 0.39-0.52. Photo-Fenton process was carried out to reduce influent toxicity that can destroy living microorganism in the MBR. Molar ratio of hydrogen peroxide to COD values ([H_2O_2/COD]), ferrous ion to hydrogen peroxide [Fe^{2+}/H_2O_2], and reaction time were studied on degradation of chemicals contained in the wastewater within the range of 1.5-2.5, 0.05-0.15 and 0-60 minutes. A statistical experimental design using central composite design (CCD) was employed to describe the relationship of individual and combined parameters towards the degradation. The optimum conditions were selected based on the highest percentage of COD and sulfide removal as well as acceptable BOD_5/COD with minimum value of molar ratio [H_2O_2/COD] and [Fe^{2+}/H_2O_2] within reaction time range. Optimum conditions for molar ratio [H_2O_2/COD] and [Fe^{2+}/H_2O_2] at pH of 3 were 1.5 and 0.05 with reaction time of 47.84 minutes. The optimum condition for MBR was evaluated based on critical flux value. It was observed that critical flux was achieved at flux of 6 and 9.5 L m^{-2} h^{-2}. The achievement of optimal conditions for both processes led to the assessment of the integrated treatment. It was found that the overall percentage removal of COD and sulfide were 99.27–99.92% and 100% leading to final effluent with COD and sulfide concentrations of 20 mg/L and 0.001 mg/L, respectively. It can be concluded that the integrated treatment system combining photo-Fenton and MBR could be an efficient alternative method for spent caustic wastewater.

ABSTRAK

Potensi sistem rawatan bersepadu yang menggabungkan proses foto-Fenton dan bioreaktor membran (MBR), telah dikaji sebagai suatu kaedah rawatan air sisa kaustik dengan nilai kepekatan awal COD dan sulfida yang berjulat 1990-2740 mg / L dan 82-165 mg/L. Proses foto-Fenton telah dilaksanakan bagi mengurangkan ketoksikan influen yang boleh memudaratkan mikroorganisma yang terdapat di dalam MBR. Nisbah molar hidrogen peroksida kepada nilai COD ([H_2O_2/COD]), ion ferus kepada hidrogen peroksida [Fe^{2+} / H_2O_2] dan masa tindakbalas telah diselidiki kesannya terhadap penguraian bahan kimia di dalam air sisa kaustik dengan julat nisbah masing-masing, iaitu 1.5-2.5, 0.05-0.15 dan 0-60 minit. Satu reka bentuk eksperimen berteraskan kaedah statistik yang digelar reka bentuk komposit berpusat (CCD), telah digunakan untuk mentafsirkan hubungan di antara pembolehubah tunggal dan gabungan terhadap penguraian air sisa kaustik. Keadaan optimum proses rawatan telah dipilih berdasarkan peratusan susutan nilai kepekatan COD dan sulfida yang tertinggi. Manakala, nilai optimum nisbah BOD_5/COD pula dikira berdasarkan kepada nisbah molar paling minimum, [H_2O_2/COD] dan [Fe^{2+} / H_2O_2] dalam kadar masa tindakbalas yang ditetapkan. Proses foto-Fenton yang optimum ialah semasa nisbah molar [H_2O_2/COD] dan [Fe^{2+} / H_2O_2] pada pH 3 adalah 1.5 dan 0.05 dengan masa tindakbalas, 47.84 minit. Selain itu, keadaan optimum bagi proses MBR pula dianggar berdasarkan nilai fluks kritikal yang diperolehi daripada ujikaji iaitu 6 dan 9.5 L m^{-2} h^{-2}. Hasil kajian ini mendapati, peratusan susutan keseluruhan nilai kepekatan COD dan sulfida adalah masing-masing sebanyak 99.27-99.92% dan 100% yang membawa kepada kepekatan akhir COD dan sulfida bagi efluen, masing-masing sebanyak 20 mg / L dan 0.001 mg / L. Oleh itu, dapat dirangkumkan bahawa sistem rawatan bersepadu yang menggabungkan proses foto-Fenton dan MBR mampu menjadi satu kaedah alternatif untuk merawat air sisa kaustik.

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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

The use of caustic solution in oil refineries and petrochemical industries to remove hydrogen sulfide and organic compounds from hydrocarbon compositions has led to the generation of large amount of spent caustic. The spent caustic wastewater are usually found in the prewashing and sweetening stages. Typically, they are categorized into two types: phenolic spent caustic and sulfidic spent caustic (Olmos *et al.*, 2004). The types of spent caustic wastewater are differentiated by their phenolic and free NaOH contents.

Most spent caustic wastewater are sent off-site to other industries that require them or are treated before disposal. For instance, in the pulp and paper industry, spent caustic was utilized in the mill's Kraft process, replacing caustic solution (Sipma *et al.*, 2004). On the other hand, spent caustic wastewater could be sent directly to the wastewater treatment plant. The conventional method of disposing spent caustic was by dumping in a deep well or ocean (Kolhatkar and Sublette, 1996; Sipma, *et al.*, 2004). This practice was not favoured because of the notorious impact of spent caustic wastewater espcially on the ecosystem. One of the physico-chemical treatment technologies that is usually employed is wet air oxidation (WAO). Generally, WAO is characterized by high temperature and pressure, with the additional high investment and maintenance costs and has safety implication.

Advanced oxidation processes have proven to be one of the most effective methods for the removal of pollutants in wastewater. Such processes include catalytic ozonation, heterogeneous photocatalysis with TiO_2, Fenton reaction and photo-Fenton reaction. Fenton and photo-Fenton have been used in many applications because of the abundance of raw materials, as well as their non-toxic nature and require low investment (Farre *et al.*, 2008). Fenton reaction involves ferrous ion and hydrogen peroxide reacting to produce hydroxyl radical (•OH) which is known to be strong in its oxidizing properties when in acidic solution. The presence of ultraviolet light, which known as photo-Fenton, will enhance the production rate of •OH, hence its efficiency is increased (Malato *et al.*, 2007).

Of recent, several studies (Bani-Melhem and Elektorowicz, 2011; Farizoglu and Keskinler, 2006; Hai *et al.*, 2012) have led to the development of a new type of membrane that gives a promising tool to treat various types of wastewater (Chen *et al.*, 2009; Mohammed *et al.*, 2008; Rosenberger *et al.*, 2002). Membrane bioreactor has become an alternative to conventional biological treatment due to its many benefits. Its characteristics that utilize micro and ultra-filtration membrane substitute the conventional sedimentation so as to produce clear effluent from the sludge. Apart from its ability to produce high quality effluent (Mohammed, *et al.*, 2008; Mutamim *et al.*, 2013), the membrane, which has porous surface of 0.2μm or less, manages to retain bacteria and viruses in the reactor (Rosenberger, *et al.*, 2002; Stephenson *et al.*, 1996).

Though there are few studies on combining biological treatment with advanced oxidation process, the integrated method that utilizes photo-Fenton and membrane bioreactor to treat spent caustic wastewater has not been reported. The goal of this study is to treat spent caustic wastewater in order to achieve maximum percentage removal of COD and sulfide at acceptable biodegradability with minimum usage of Fenton reagents. It is believed that spent caustic wastewater could be treated properly in this way to meet with standard quality requirements and which can then be implemented in real wastewater treatment plant.

1.2 Statement of Problems

The negative environmental impacts of spent caustic wastewater on human health have been reported (Abdulah *et al.*, 2011; B. Kumfer, 2010; de Graaff *et al.*, 2011; de Graaff *et al.*, 2012; Felix Davila, 2007). The confirmation on the toxic effect has been outlined in Environmental Quality Act Regulation under category 4 scheduled waste SW 402 which usually contains corrosive or hazardous waste where it is commonly disposed to a licensed off-site recycler (Malaysia, 1979). This also in line with US Resources Conservation and Recovery Act that assigned spent caustic under D003 (reactive sulfide) hazardous waste (Sheu and Weng, 2001). Wet air oxidation is the existing treatment process for caustic wastewater. However, its operating condition requires high pressure and temperatures and it is one of its drawbacks in terms of safety and costs. Few studies have been done to find alternative treatment methods for spent caustic, like coagulation (Demirci *et al.*, 1998) and electrochemical process (Yan *et al.*, 2011). However, the methods are characterized by low removal of COD and very low rates of reaction which restrict their application (Demirci, *et al.*, 1998; Diya'uddeen *et al.*, 2011). Another factor is the single nature of the treatment methods studied. This study proposed an integrated system that consists of chemical treatment (photo-Fenton) and biological treatment (membrane bioreactor) which are expected to synergitically give high quality effluent when compared with single process. Furthermore, the integrated treatment will also serve as reference for further investigation with regard to the combination of Fenton and biological processes and the ability of microbes to withstand wastewater that has been chemically treated using the photo-Fenton process.

1.3 Objectives of the study

The following are the objectives of the study:

(i) To obtain optimum operating parameters (reaction time, dosage of oxidant and dosage of catalyst) for photo-Fenton process for synthetic spent caustic wastewater;

(ii) To assess the effect of photo-Fenton optimum conditions on biomass and membrane;

(iii) To obtain optimum operating condition for membrane bioreactor prior to integration of treatment system employing photo-Fenton and membrane bioreactor for treating synthetic spent caustic wastewater.

1.4 Scope of the Study

The study was conducted within the scope specified below:

- The optimum operating condition for photo-Fenton process were evaluated based on highest percentage removal of chemical oxygen demand (COD) and sulfide removal with acceptable biodegradability level. In this study, the amounts of oxidant and catalyst as well as reaction time were chosen to be the operating conditions for photo-Fenton process. Response surface methodology (RSM) and the method of Central Composite Design (CCD) were implemented in this study using Design-Expert Software;
- The optimum operating condition for membrane bioreactor was determined using flux-stepping method. Critical flux was achieved in order to avoid

membrane biofouling where cleaning will be needed. The value of flux that is below the critical flux represent the operating condition. Besides, membrane bioreactor study was conducted at short-term operation where sludge retention time and biofoulant will not be studied and the membrane will undergo a one-time operation;

- Theoratically, photo-Fenton process will generate free radicals to degrade the organic compounds into simpler species. Although it has an advantage in degradation process, the concern on free radical compounds arises on whether they are toxic to the microbes. To solve the problem, acclimatization was employed as the source of microbial toxicity measurement. As for the effect of free radicals on membrane, investigation of surface morphology will be implemented. Scanning electron microscope (SEM) was used to provide qualitative justification;
- Based on the individual treatment, the optimum operating conditions and results obtained act as basis to the integrated system. The integrated treatment is assumed to be well-mixed and the performance was evaluated based on removal of COD, BOD and sulfide concentrations. The chosen parameters were analyzed on selected locations that are: (i) before entering the chemical treatment, (ii) after undergoing chemical treatment and (iii) after undergoing chemical and biological treatment. The selected parameters were compared with standard parameters assigned under the Environmental Quality (Industrial Effluent) Regulation 2009.

1.5 Significance of the Study

This research serves as new route to treat spent caustic wastewater as it gives more benefits in comparison to the existing technology. It also contributes to the development of treatment technology for treating high strength wastewater. The system also employs in-situ treatment with use of smaller areas as compared to conventional treatment, which plays a significant role in selecting the treatment plant. Since the system is operated at ambient conditions, it involves lower costs in terms of construction and maintenance. In addition, safety concern will be at a high priority compared with existing treatment that need to function at high temperature and pressure. The ability of the integrated system to treat spent caustic wastewater will serve as evidence in employing it in real wastewater treatment plants.

On the study of the toxic effect of the free radical on membrane, the result will give an overview and new findings for further research. The ability of the biomass to adapt with free radicals environment will be analysed. Finally, the justification of using a membrane that is chemically treated with photo-Fenton for wastewater treatment will have been established.

1.6 Thesis Layout

This thesis consists of five chapters. Each of the chapters will be briefly discussed and they are interrelated to each other bounded by the scope of study.

Chapter 1 deals with the overview of wastewater treatment and technologies that have been implemented highlighting its drawbacks provide the need of the study. Therefore, an alternative is proposed concerning the specific problem which has been addressed in the objectives of the study.

Chapter 2 is a literature review on the characteristics of wastewater and covers physical and chemical characteristics of spent caustic wastewater. It also discuss the method have been carried out in the treatment of spent caustic wastewater. The factors that affect the process were addressed in this chapter.

Chapter 3 describes the methods and technique chosen to be implemented in this study. Samples were taken for analysis and all the analytical methods are described in this chapter.

Chapter 4 is the full result of this study. The parameters that contribute and give impact to the study will be discussed. Each of the result will be trasformed into simplified graph for further clarification.

Chapter 5 is the conclusion obtained from the study. It gives an insight on how the objectives have been met. The chapter ends with suggestions that were made for future research.

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